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## (54) DISCHARGE METHOD FOR LITHIUM SECONDARY BATTERY

## (57)Abstract:

PURPOSE: To prevent deteriorating a battery characteristic and worsening thermal stability due to repeated charge/discharge by performing the prescribed initial discharge at the time of ending the charge or starting the discharge, in a lithium secondary battery using a lithium metal for its negative pole.

CONSTITUTION: At the time of ending a charge or starting a discharge of a battery, the initial discharge within 30 seconds is performed by current density of 5mA/cm<sup>2</sup> or more per unit area of a positive or negative pole. A uniform fine hole is opened to a protective film formed in a lithium surface by the discharge of large current thus performed, and in the case of low current discharge thereafter, lithium is uniformly fused to remove the protective film. Thus by preventing producing needle-shaped lithium due to local deposition in the case of charge thereafter, a charge/discharge life and thermal stability are improved. Further by increasing current density of the initial discharge, a discharge time can be shortened.

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(54)【発明の名称】 リチウム二次電池の放電方法

(57)【要約】

【目的】 リチウム負極に起因する充放電の繰返しに伴う電池特性の劣化と、熱安定性の低下の問題を解決するためのリチウム二次電池の放電方法を提供する。

【構成】 電池の充電終了時または、放電開始時に前記正極あるいは前記負極の単位面積あたり  $5 \text{ mA} / \text{cm}^2$  以上の電流密度で、30秒間以内の初期放電を行なうことを特徴とする。

【効果】 電池の充放電サイクル寿命を向上することができ、また、針状の析出形態が生じないので、その工業的価値は極めて大である。

## 【特許請求の範囲】

【請求項1】正極と、リチウム金属を負極とするリチウム二次電池の放電方法において、電池の充電終了時または、放電開始時に前記正極あるいは前記負極の単位面積あたり  $5 \text{ mA} / \text{cm}^2$  以上の電流密度で、30 秒間以内の初期放電を行なうことを特徴とするリチウム二次電池の放電方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明はリチウム電池の放電方法、さらに詳しくはリチウムイオンを挿入、脱離できる正極と、リチウム金属あるいはリチウム合金を用いた負極と、非水電解液よりなる、充放電可能なリチウム二次電池の電池特性を低下せしめない放電方法に関するものである。

## 【0002】

【従来の技術】電子機器の小型軽量化、携帯化が進み、その電源として充放電可能な高エネルギー密度電池の開発が要請されている。負極としてリチウム金属、アルミニウム等とのリチウム合金、または炭素等のリチウムイオンを放出、吸収する電極を用い、リチウムイオンを挿入、脱離できる正極と、非水電解液とを用いた、いわゆるリチウム二次電池は、軽量で取得電圧が高いという特徴を有するため、上記小型軽量化した電子機器の要求に応える電池として、開発が進められている。

【0003】リチウム二次電池の負極材料は、リチウム合金や、炭素等のリチウムイオンを放出、吸収する電極を用いた場合よりも、リチウム金属を用いた場合の法が、単位重量当たりおよび単位体積当たりのエネルギー（ワット時）が大きくなる。しかしながら、リチウム金属を負極に用いたリチウム二次電池においては、充電により樹枝状のリチウムが析出し、負極集電体から欠落する等の理由により、充放電寿命が短く、かつ充放電の繰り返しの伴うリチウム表面積の増加による熱安定性の低下が問題となっている。この充放電寿命の劣化は、電池の3時間率充電（電池の全容量を3時間で充電できる電流値による充電）相当の電流値以上の電流値による充電や、10時間率放電（電池の容量を10時間で放電できる電流値による放電）に相当する電流値以下の電流値による放電等で顕著になる（例えば、F.C. Laman, J. Power Sources, 24, 195 (1988)）。

【0004】これらの充放電寿命の劣化が起こる原因は、リチウムの析出形態に依存することが知られている、すなわち、粒子状の析出形態よりも針状の析出形態がリチウム二次電池としての充放電サイクル寿命の低下をもたらしているのである（M. Arakawa, Extended Abstracts of 6th IMLB, p-6 (1992)）。リチウムの析出形態を制御し、充放電寿命を長くする試みとしては、例えば、電解液に添加剤を加え、添加剤とリチウムの相互作用により、リチウム析出の形態を制御する方法（例え

ば、J.O.Besenhard, J. Power Sources, 20, 253 (1987)や、中村、第28回電池討論会予稿集, p-191 (1987)）や、リチウムの電析時に圧力を加えて析出形態を制御する方法（UK Patent GB 2 105 512 A）等報告されているが、未だ十分な充放電サイクル寿命を得るに至っていない。

## 【0005】

【発明が解決しようとする問題点】本発明は、リチウム金属、あるいはリチウム金属を構成成分に含む複合電極、あるいはリチウム合金よりなる負極を用いたリチウム二次電池において、リチウム負極に起因する充放電の繰り返しの伴う電池特性の劣化と、熱安定性の低下の問題を解決するためのものである。

## 【0006】

【問題を解決するための手段】上記問題点を解決するため、本発明によるリチウム二次電池の放電方法は、正極と、リチウム金属を負極とするリチウム二次電池の放電方法において、電池の充電終了時または、放電開始時に前記正極あるいは前記負極の単位面積あたり  $5 \text{ mA} / \text{cm}^2$  以上の電流密度で、30 秒間以内の初期放電を行なうことを特徴とする。

【0007】リチウム二次電池の充放電サイクル寿命は、電池の充電電流密度に大きく依存する。 $0.5 \text{ mA} / \text{cm}^2$ 未満の低電流放電では、放電に伴うリチウムの溶出がインピーダンスの相対的に小さい部位に集中し、すなわち局部的に起こる。これに対して、 $0.5 \text{ mA} / \text{cm}^2$ 大電流放電では、リチウムは比較的広い範囲に渡って均一に溶出していた。この放電時のリチウムの溶出状態が、次の充電時の析出形態に影響していた。低電流放電に続く充電では、リチウムの析出は専ら局部的にリチウムの溶出した部位に集中し、したがって実質的には、この部位における電流密度が高くなるため、針状のリチウムが析出した。これに対し、大電流放電後の充電では、リチウムの析出が広い範囲に渡って起こり、実質的な電流密度が低くなり、粒子状形態のリチウムが析出した。この充電時の析出形態の違いおよび、圧力のかかり方の違い（低電流放電の方が、不均一に析出するためリチウム表面への力が局部的にしか生じず、したがって圧力による形態改善の効果も少ない）により、低電流放電を行なった電池では充放電寿命が劣化すると共に熱安定性が低下していた。したがって、低電流放電による熱安定性の低下は、リチウム金属表面に電池を作る以前から存在した表面膜（Native Film）あるいは、リチウムと電解液との反応によりリチウム表面に形成された保護膜の存在に起因する、リチウムの局部的溶出が原因と考えられる。

【0008】一方、大電流放電を行なうと、電極に大きな過電圧が付与されるため、保護膜の不均一性に起因するリチウム表面のインピーダンスの大小がキャンセルされ、均一なリチウムの溶出が起こる。したがって、大電

流パルスによりリチウム表面に均一な細孔が開くと、それに続いて低電流放電を行なっても、細孔に添ってリチウムが溶出し、結果的にはリチウムの均一な溶出が広範囲に渡って起こる。保護膜を除去し均一なエッチングを行なうことにより、リチウム析出形態が改善され結果的に充放電寿命と熱安定性の向上につながる。以上の知見に基づいて、本発明に至ったものである。

【0009】すなわち、リチウム金属を負極とするリチウム二次電池の放電方法において、電池の充電終了時または、放電開始時に正極あるいは負極の単位面積当たり  $5 \text{ mA/cm}^2$  以上の電流密度で、30秒間以内の初期放電を行なうことによって、充放電サイクルに伴う電池特性低下の原因となっている針状析出形態の析出が抑制されるのである。

【0010】本発明においては、放電開始次のリチウム負極表面の形態が重要であるので、本発明による方法の実施は、放電開始時であってもよいし、放電の前の充電が終了した後であってもよい。すなわち、放電前であれば、本発明の方法の実施のとき（タイミング）は、特に限定はされない。

【0011】本発明の放電における電流密度については、 $5 \text{ mA/cm}^2$  未満では上述したように針状リチウムの析出が抑制されるという本発明特有の効果が現れない。リチウムの析出形態の点から、電流密度は高いほ

表1

| 電池番号 | パルス電流<br>(mA/cm <sup>2</sup> ) | パルス時間<br>(秒) | 放電電流<br>(mA/cm <sup>2</sup> ) | 放電時間<br>(分) |
|------|--------------------------------|--------------|-------------------------------|-------------|
| 1    | 10                             | 30           | 0.2                           | 1475        |
| 2    | 25                             | 12           | 0.2                           | 1475        |
| 3    | 50                             | 6            | 0.2                           | 1475        |
| 4    | —                              | —            | 0.2                           | 1500        |

【0015】図2、図3、図4、図5は、それぞれ電池番号1、2、3、4における、リチウム溶出後の負極形態のSEM写真を示したものである。図2～図4は電池番号1～3をそれぞれ10、25、50 mA/cm<sup>2</sup>の電流密度で30、12および6秒間放電した後、0.2 mA/cm<sup>2</sup>で放電を行ない、負極形態を走査型電子顕微鏡（SEM）により観察した写真である。

【0016】写真よりわかるように、大電流パルスを実施しなかった電池（図5）のリチウム負極では局部的溶

出が起きているが、それぞれ、10、25、50 mA/cm<sup>2</sup>で数秒放電した後、0.2 mA/cm<sup>2</sup>放電したリチウム負極（図2～図4）では、パルス電流値が高くなるほど、均一な溶出が起きている。

【0012】本発明の放電方法は、リチウム二次電池の実際の使用状況において、0.5 mA/cm<sup>2</sup>以下の低電流で放電が行なわれる場合に、特に顕著な効果が得られるが、0.5 mA/cm<sup>2</sup>以上の例えば1時間率放電（電池の全容量を1時間で放電できる電流値による放電）においても悪影響を及ぼすことなく、さらに充放電寿命を改善する効果がある。

【0013】

【実施例1】負極にリチウムを圧着したコイン型電池（図1）を作製し、以下に示す放電条件でリチウムの溶出を行なった後、走査型電子顕微鏡（SEM）による負極形態の観察を行なった。図1中、aは正極ケース、bは負極ケース、cはガスケット、dは厚さ70 μmリチウム箔（負極）、eは厚さ0.4 mmのステンレス網製円盤（正極）、fはポリプロピレン製セパレータである。

【0014】

出が起きているが、それぞれ、10、25、50 mA/cm<sup>2</sup>で数秒放電した後、0.2 mA/cm<sup>2</sup>放電したリチウム負極（図2～図4）では、パルス電流値が高くなるほど、均一な溶出が起きている。

【0017】

【実施例2】図1に示したコイン型電池を用い、以下の条件でリチウムの溶出後、析出させたリチウム負極のSEMによる観察を行なった。

【0018】

表2

| 電池<br>番号 | パルス電流<br>(mA/cm <sup>2</sup> ) | パルス<br>時間(秒) | 放電電流<br>(mA/cm <sup>2</sup> ) | 放電<br>時間(分) | 充電電流<br>(mA/cm <sup>2</sup> ) | 充電<br>時間(分) |
|----------|--------------------------------|--------------|-------------------------------|-------------|-------------------------------|-------------|
| 5        | 50                             | 6            | 0.2                           | 1475        | 0.4                           | 750         |
| 6        | —                              | —            | 0.2                           | 1500        | 0.4                           | 750         |

【0019】図6、図7はそれぞれ電池番号5、6におけるリチウム析出後の負極形態のSEM写真を示したものである。図6は50 mA/cm<sup>2</sup>の電流密度で6秒間放電した後、0.2 mA/cm<sup>2</sup>で放電し、さらに0.4 mA/cm<sup>2</sup>で充電した負極の形態をSEMにより観察した写真である(電池番号5)。写真より、大電流で数秒間放電した電池5の負極(図6)では、極めてスムーズなリチウムの析出が起こっているのに対し、低電流放電のみの電池6の負極(図7)では、充放電サイクル寿命を劣化する針状の形態が析出していることが認められる。

#### 【0020】

【実施例3】正極活物質に非晶質V<sub>2</sub>O<sub>5</sub>、負極にリチウム金属を用い、炭酸エチレンと2-メチルテトラヒドロフランの混合溶媒にLiAsF<sub>6</sub>を1.5 M溶解した電解液を用いたコイン型電池(図8)において、0.2 mA/cm<sup>2</sup>で放電し、0.4 mA/cm<sup>2</sup>で充電するサイクルを繰り返した場合(電池7)と、0.2 mA/cm<sup>2</sup>で放電する前に、50 mA/cm<sup>2</sup>の電流密度で約10秒放電した場合(電池8)について、充放電寿命の比較を行なった。図8中、aは正極ケース、bは負極ケース、cはガasket、dは厚さ70 μmリチウム箔(負極)、eは非晶質V<sub>2</sub>O<sub>5</sub>を活物質とした正極、fはポリプロピレン製セパレータである。

【0021】図9は電池の充放電サイクル数と、充放電サイクル初期における最高容量を1.0としたときの相対電池容量との関係を示した図である。この図9より、低電流放電前に大電流パルス放電を行なった場合には、低電流放電のみの場合に比べ、50サイクル以降の急激な容量低下が見られず、良好な充放電寿命を有することがわかる。

#### 【0022】

【実施例4】正極活物質にMoS<sub>2</sub>を用い、負極にリチウム金属を用い、炭酸エチレンと炭酸プロピレンの混合溶媒に、LiAsF<sub>6</sub>を1 M溶解させた電解液を用いた、円筒型炭酸電池(図10)において、0.2 mA/cm<sup>2</sup>で放電し、0.4 mA/cm<sup>2</sup>で充電するサイクルを繰り返した場合(電池9)と、0.2 mA/cm<sup>2</sup>で放電する前に、25 mA/cm<sup>2</sup>の電流密度で約10秒間放電した場合(電池10)について、充放電寿命の比較を行なった。図10中、gは正極キャップ、hは正極

タブ、iは負極タブ、kは正極、lはセパレータ、mは負極、nは負極缶である。

【0023】図11は電池の充放電サイクル数と、充放電サイクル初期における最高容量を1.0としたときの相対電池容量との関係を示した図である。この図11より、0.2 mA/cm<sup>2</sup>の低電流放電前に25 mA/cm<sup>2</sup>の大電流パルス放電を行なった場合には、低電流放電のみの場合に比べ、50サイクル以降のソフトショート(針状あるいは樹枝状のリチウムがセパレータを貫通し正極と負極が穏やかな短絡状態になること)が見られず、良好な充放電寿命を有することがわかる。

#### 【0024】

【発明の効果】以上示したように、リチウム金属を用いるリチウム二次電池において、本発明によって電池の充放電サイクル寿命を向上することができ、また、針状の析出形態が生じないので、その工業的価値は極めて大である。

#### 【図面の簡単な説明】

【図1】実施例、比較例で用いたコイン型電池の一部断面図。

【図2】10 mA/cm<sup>2</sup>の電流密度で30秒間放電した後、0.2 mA/cm<sup>2</sup>で放電を行なった負極形態の走査型電子顕微鏡写真。

【図3】25 mA/cm<sup>2</sup>の電流密度で12秒間放電した後、0.2 mA/cm<sup>2</sup>で放電を行なった負極形態の走査型電子顕微鏡写真。

【図4】50 mA/cm<sup>2</sup>の電流密度で6秒間放電した後、0.2 mA/cm<sup>2</sup>で放電を行なった負極形態の走査型電子顕微鏡写真。

【図5】従来の0.2 mA/cm<sup>2</sup>のみの放電を行なったときの負極形態の走査型電子顕微鏡写真。

【図6】50 mA/cm<sup>2</sup>の電流密度で6秒間放電した後、0.2 mA/cm<sup>2</sup>で放電し、さらに0.4 mA/cm<sup>2</sup>で充電した負極形態の走査型電子顕微鏡写真。

【図7】従来の0.2 mA/cm<sup>2</sup>で放電した後、0.4 mA/cm<sup>2</sup>で充電した負極形態の走査型電子顕微鏡写真。

【図8】実施例、比較例に用いたコイン型電池の一部断面図。

【図9】電池の充放電サイクル数と、充放電サイクル初期における最高容量を1.0としたときの相対電池容量

との関係を示した図。

【図10】実施例、比較例に用いた円筒型電池の構造図。

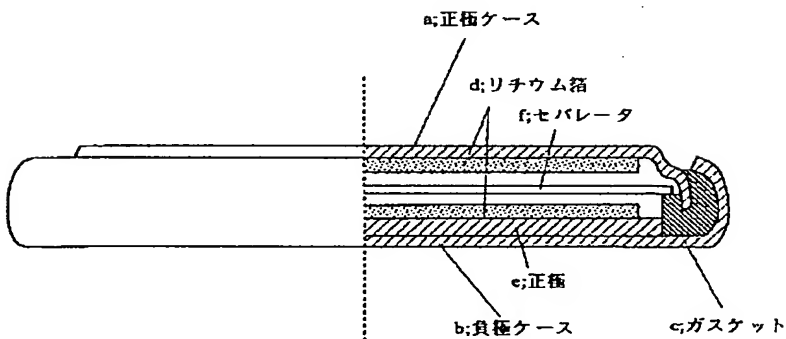
【図11】電池の充放電サイクル数と、充放電サイクル初期における最高容量を1.0としたときの相対電池容量との関係を示した図。

【符号の説明】

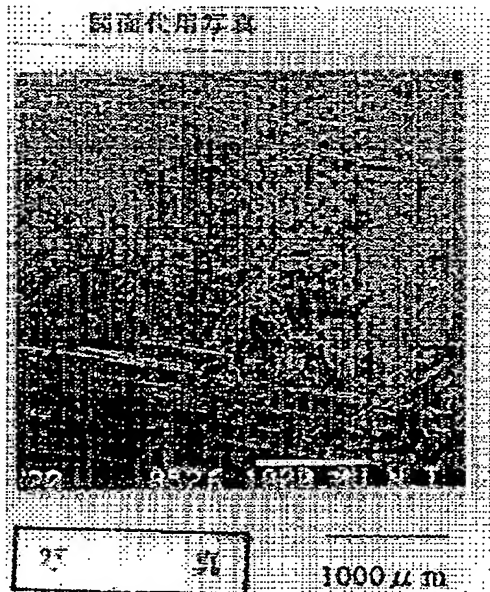
- a 正極ケース
- b 負極ケース
- c ガasket

- d リチウム箔
- e 正極
- f ポリプロピレン製セパレータ
- g 正極キャップ
- h 正極タブ
- i 負極タブ
- k 正極
- l セパレータ
- m 負極
- n 負極缶

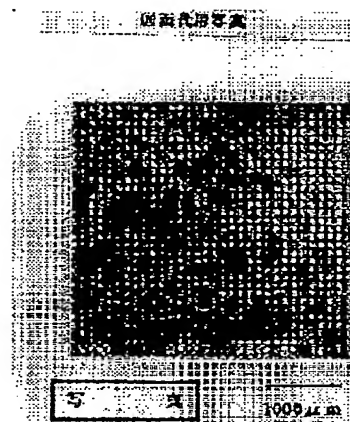
【図1】



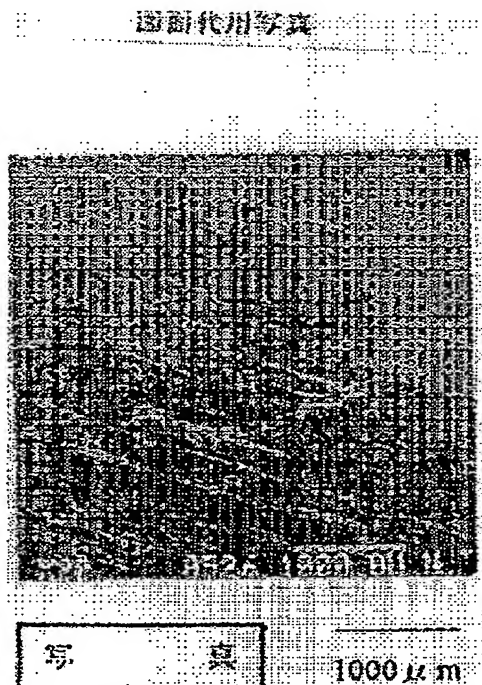
【図3】



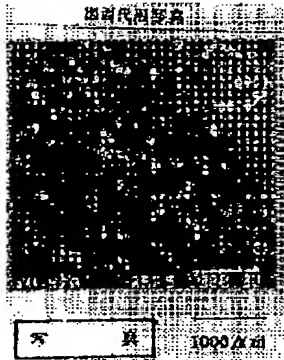
【図2】



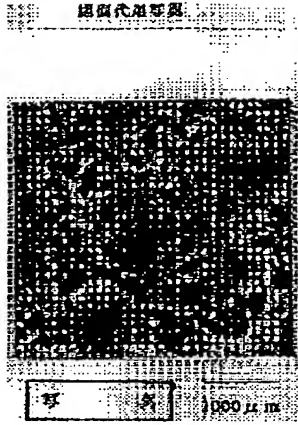
【図4】



【図5】



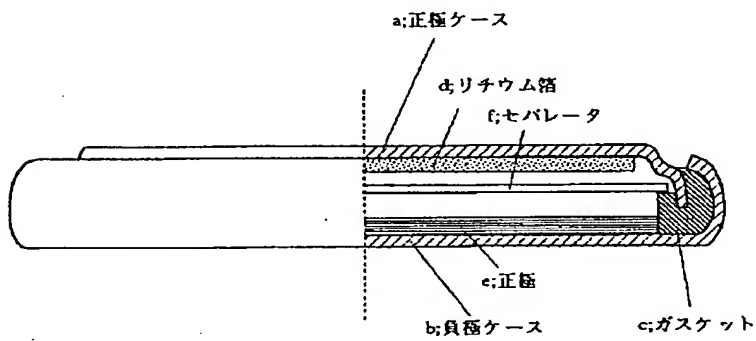
【図6】



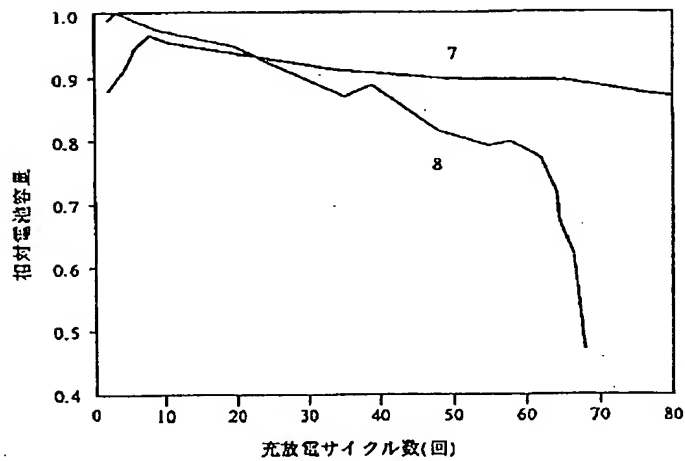
【図7】



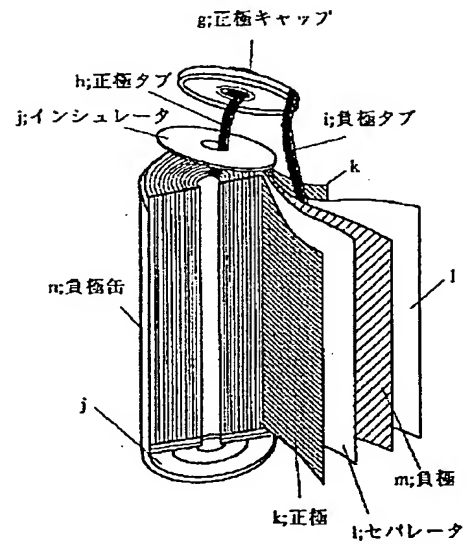
【図8】



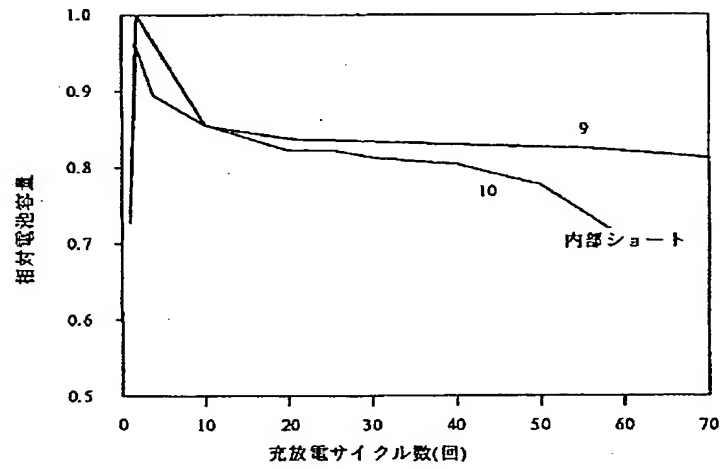
【図9】



【図10】



【図11】



フロント ページの続き

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**CLAIMS**

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[Claim(s)]

[Claim 1] The discharge approach of the lithium secondary battery characterized by performing initial discharge within for 30 seconds with two or more 5 mA/cm [ per unit area of said positive electrode or said negative electrode ] current density at the time of charge termination of a cell, or discharge starting in the discharge approach of a positive electrode and the lithium secondary battery which uses a lithium metal as a negative electrode.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the discharge approach of not making the cell property of the lithium secondary battery which serves as the discharge approach of a lithium cell, a positive electrode from which a lithium ion can be inserted and it can be desorbed in more detail, and a negative electrode which used the lithium metal or the lithium alloy from nonaqueous electrolyte and in which charge and discharge are possible falling.

[0002]

[Description of the Prior Art] The formation of small lightweight of electronic equipment and carrying-ization progress, and development of the high energy consistency cell in which charge and discharge are possible as the power source is demanded. The electrode which emits lithium ions, such as a lithium alloy with a lithium metal, aluminum, etc. or carbon, and is absorbed as a negative electrode is used, and since it has the description using the positive electrode which can insert a lithium ion and can be desorbed from it, and nonaqueous electrolyte that the so-called lithium secondary battery is lightweight, and an acquisition electrical potential difference is high, development is furthered as a cell which meets the demand of the electronic equipment above-formed into small lightweight.

[0003] Per unit weight and the energy per unit volume (watt-hour) become [ the law at the time of using a lithium metal ] large rather than the case where the electrode which the negative-electrode ingredient of a lithium secondary battery emits a lithium alloy and lithium ions, such as carbon, and is absorbed is used. However, in the lithium secondary battery which used the lithium metal for the negative electrode, the lithium of arborescence deposits by charge, for the reason missing from a negative-electrode charge collector, a charge-and-discharge life is short, and the fall of the thermal stability by the increment in the lithium surface area accompanying the repeat of charge and discharge poses a problem. Degradation of this charge-and-discharge life becomes remarkable by charge by the current value beyond a current value equivalent to the rate charge of 3 time amount of a cell (charge by the current value which can charge the full capacity of a cell in 3 hours), discharge by the current value below the current value equivalent to the rate discharge of 10 time amount (discharge by the current value which can discharge the capacity of a cell in 10 hours), etc. (for example, F.C.Laman, J.Power Sources, 24, and 195 (1988)).

[0004] Depending on the deposit gestalt of a lithium for the cause by which degradation of these charge-and-discharge lives takes place is known, namely, the deposit gestalt more nearly needlelike than a particle-like deposit gestalt has brought about the fall of the charge-and-discharge cycle life as a lithium secondary battery (M.Arakawa, Extended Abstracts of 6th IMLB, and p-6 (1992)). As an attempt which controls the deposit gestalt of a lithium and lengthens a charge-and-discharge life An

additive is added to the electrolytic solution. For example, by the interaction of an additive and a lithium the approach (J.O.Besenhard, J.Power Sources, 20, and 253 (1987) --) of controlling the gestalt of a lithium deposit [ for example, ] Although Nakamura, the collection of the 28th cell debate drafts, p-191 (1987), the approach (UK Patent GB 2 105 512 A) of applying a pressure at the time of the electrocrystallization of a lithium, and controlling a deposit gestalt, etc. are reported, it has come to acquire still sufficient charge-and-discharge cycle life.

[0005]

[Problem(s) to be Solved by the Invention] This invention is for solving degradation of the cell property accompanying the repeat of the charge and discharge resulting from a lithium negative electrode, and the problem of a fall of thermal stability in the lithium secondary battery using the composite electrode which contains a lithium metal or a lithium metal in a constituent, or the negative electrode which consists of a lithium alloy.

[0006]

[Means for Solving the Problem] In order to solve the above-mentioned trouble, in the discharge approach of a positive electrode and the lithium secondary battery which uses a lithium metal as a negative electrode, at the time of charge termination of a cell, or discharge starting, the discharge approach of the lithium secondary battery by this invention is two or more 5 mA/cm [ per unit area of said positive electrode or said negative electrode ] current density, and is characterized by performing initial discharge within for 30 seconds.

[0007] It depends for the charge-and-discharge cycle life of a lithium secondary battery on the charging current consistency of a cell greatly. In less than two 0.5 mA/cm low current discharge, the elution of the lithium accompanying discharge concentrates on a small part relatively [ an impedance ], namely, it happens locally. On the other hand, in 0.5 mA/cm<sup>2</sup> high-current discharge, the lithium was crossed to the comparatively large range and eluted in homogeneity. The elution condition of the lithium at the time of this discharge had influenced the deposit gestalt at the time of the next charge. In charge following low current discharge, the deposit of a lithium was concentrated on the part to which the lithium was eluted locally chiefly, therefore since the current density in this part became high substantially, the needlelike lithium deposited. On the other hand, in the charge after high current discharge, the deposit of a lithium crossed to the large range, and took place, substantial current density became low, and the lithium of a particle-like gestalt deposited. The difference in the deposit gestalt at the time of this charge and the pressure were applied, and by the difference (since the direction of low current discharge deposits in an ununiformity, the force on the front face of a lithium does not arise locally, therefore there is also little effectiveness of the gestalt improvement by the pressure) of the direction, by the cell which performed low current discharge, while the charge-and-discharge life deteriorated, thermal stability was falling. Therefore, before the fall of the thermal stability by low current discharge makes a cell to a lithium surface of metal, the local elution of a lithium resulting from existence of the membrane surface (Native Film) which existed [ from ], or the protective coat formed in the lithium front face of the reaction of a lithium and the electrolytic solution is considered to be the cause.

[0008] On the other hand, if high current discharge is performed, since a big overvoltage will be given to an electrode, the size of the impedance on the front face of a lithium resulting from the heterogeneity of a protective coat is canceled, and the elution of a uniform lithium happens. Therefore, if uniform pore opens to a lithium front face by the high current pulse, even if it performs low current discharge following it, pore is accompanied, a lithium is eluted, and as a result, the uniform elution of a lithium will cross broadly and will happen. By removing a protective coat and performing uniform etching, a lithium deposit gestalt is improved and it leads to improvement in a charge-and-discharge life and thermal stability as a result. It results in this invention based on the above knowledge.

[0009] That is, in the discharge approach of the lithium secondary battery which uses a lithium metal as a negative electrode, the deposit of the needlelike deposit gestalt leading to the cell property fall accompanying a charge-and-discharge cycle is controlled by being two or more 5 mA/cm [ per unit area of a positive electrode or a negative electrode ] current density, and performing initial discharge within for 30 seconds at the time of charge termination of a cell, or discharge starting.

[0010] this invention -- setting -- discharge starting -- since the gestalt of the next lithium negative-electrode front face is important, you may be operation of the approach by this invention at the discharge-starting time, and after the charge before discharge is completed, it may be. Namely, if it is before discharge, especially limitation will not be carried out at the time of operation of the approach of this invention (timing).

[0011] About the current density in discharge of this invention, the effectiveness peculiar to this invention that a deposit of a needlelike lithium is controlled as mentioned above does not show up in less than two 5 mA/cm. From the point of the deposit gestalt of a lithium, although it is that current density is so desirable that it is high as effectiveness of this invention, it is necessary to shorten time amount of the initial discharge from the point of consumption of the energy which generation of heat of a cell and a cell have, so that current density increases. If it is about two 5 mA/cm current density, a 30-second room [ about ] initial charging time value is enough. An initial charging time value can be shortened from for 30 seconds, so that current density is made high.

[0012] In the actual operating condition of a lithium secondary battery, the discharge approach of this invention is effective in not doing a bad influence in two or more 0.5 mA/cm (discharge by the current value which can discharge the full capacity of a cell in 1 hour), for example, the rate discharge of 1 time amount, and improving a charge-and-discharge life further, although remarkable effectiveness is especially acquired when discharge is performed by the low current of two or less [ 0.5mA //cm ].

[0013]

[Example 1] The coin mold cell ( drawing 1 ) which stuck the lithium to the negative electrode by pressure was produced, and after performing elution of a lithium on the discharge conditions shown below, the negative-electrode gestalt by the scanning electron microscope (SEM) was observed. For a negative-electrode case and c, a gasket and d are [ a / a positive-electrode case and b / the disk made from a stainless steel network with a thickness of 0.4mm (positive electrode) and f of 70 micrometer lithium foil (negative electrode) in thickness and e ] the separators made from polypropylene among drawing 1 .

[0014]

表 1

| 電池<br>番号 | パルス電流<br>(mA/cm <sup>2</sup> ) | パルス時間<br>(秒) | 放電電流<br>(mA/cm <sup>2</sup> ) | 放電時間<br>(分) |
|----------|--------------------------------|--------------|-------------------------------|-------------|
| 1        | 10                             | 30           | 0.2                           | 1475        |
| 2        | 25                             | 12           | 0.2                           | 1475        |
| 3        | 50                             | 6            | 0.2                           | 1475        |
| 4        | —                              | —            | 0.2                           | 1500        |

[0015] Drawing 2 , drawing 3 , drawing 4 , and drawing 5 show the SEM photograph of the negative-electrode gestalt after lithium elution in the cell numbers 1, 2, 3, and 4, respectively. Drawing 2 - drawing 4 are 10 and the photograph which discharged by 0.2 mA/cm<sup>2</sup> with the current density of 2 cm 25 or 50mA /30, 12, and after discharging for 6 seconds, and observed the negative-electrode gestalt with the scanning electron microscope (SEM) about the cell numbers 1-3, respectively.

[0016] In the lithium negative electrode of the cell ( drawing 5 ) which did not carry out a high current pulse, local elution has happened so that a photograph may show, but with the lithium negative electrode ( drawing 2 - drawing 4 ) which discharged two times 0.2 mA/cm, after discharging several seconds by 10, 25, and 50 mA/cm<sup>2</sup>, uniform elution has happened, respectively, so that a pulse current value becomes high.

[0017]

[Example 2] Observation by SEM of the deposited lithium negative electrode was performed after the elution of a lithium on condition that the following using the coin mold cell shown in drawing 1 .

[0018]

表 2

| 電池<br>番号 | パルス電流<br>(mA/cm <sup>2</sup> ) | パルス<br>時間(秒) | 放電電流<br>(mA/cm <sup>2</sup> ) | 放電<br>時間(分) | 充電電流<br>(mA/cm <sup>2</sup> ) | 充電<br>時間(分) |
|----------|--------------------------------|--------------|-------------------------------|-------------|-------------------------------|-------------|
| 5        | 50                             | 6            | 0.2                           | 1475        | 0.4                           | 750         |
| 6        | —                              | —            | 0.2                           | 1500        | 0.4                           | 750         |

[0019] Drawing 6 and drawing 7 show the SEM photograph of the negative-electrode gestalt after the lithium deposit in the cell numbers 5 and 6, respectively. After 50mA /of drawing 6 discharges for 6 seconds with the current density of 2 cm, they is the photograph which observed the gestalt of the negative electrode which discharged by 0.2 mA/cm<sup>2</sup> and charged the pan by 0.4 mA/cm<sup>2</sup> by SEM (cell number 5). From a photograph, it is admitted with the negative electrode ( drawing 7 ) of the cell 6 of only low current discharge to the deposit of a very smooth lithium having taken place according to the high current with the negative electrode ( drawing 6 ) of the cell 5 which discharged for several seconds that the needlelike gestalt which deteriorates a charge-and-discharge cycle life deposits.

[0020]

[Example 3] In the coin mold cell ( drawing 8 ) using the electrolytic solution which used amorphous substance V2O5 for positive active material, used the lithium metal for the negative electrode, and dissolved LiAsF6 in ethylene carbonate and the mixed solvent of 2-methyl tetrahydrofuran 1.5M The charge-and-discharge life was compared about the case (cell 7) where the cycle which discharges by 0.2 mA/cm<sup>2</sup> and is charged by 0.4 mA/cm<sup>2</sup> is repeated, and the case (cell 8) where it discharges for about 10 seconds with the current density of 50 mA/cm<sup>2</sup> before discharging by 0.2 mA/cm<sup>2</sup>. A positive-electrode case, the positive electrode with which in b a gasket and d used amorphous substance V2O5 as 70-micrometer lithium foil (negative electrode) in thickness, and a negative-electrode case and c used e as the active material, and f of a are the separators made from polypropylene among drawing 8 .

[0021] Drawing 9 is drawing having shown the relation between the number of charge-and-discharge cycles of a cell, and the relative cell capacity when setting the highest capacity in the early stages of a charge-and-discharge cycle to 1.0. This drawing 9 shows the rapid capacity fall after 50 cycles

not being seen, but having a good charge-and-discharge life compared with the case of only low current discharge, in the case where a high current pulse discharge is performed before low current discharge.

[0022]

[Example 4] In the cylindrical carbonic acid cell ( drawing 10 ) using the electrolytic solution which used MoS<sub>2</sub> for positive active material, used the lithium metal for the negative electrode, and was made to dissolve LiAsF<sub>6</sub> in the mixed solvent of ethylene carbonate and propylene carbonate 1M The charge-and-discharge life was compared about the case (cell 9) where the cycle which discharges by 0.2 mA/cm<sup>2</sup> and is charged by 0.4 mA/cm<sup>2</sup> is repeated, and the case (cell 10) where it discharges for about 10 seconds with the current density of 25 mA/cm<sup>2</sup> before discharging by 0.2 mA/cm<sup>2</sup>. the inside of drawing 10 , and g --- for a negative-electrode tab and k, a positive electrode and l are [ a positive-electrode cap and h / a positive-electrode tab and i / a negative electrode and n of a separator and m ] negative-electrode cans.

[0023] Drawing 11 is drawing having shown the relation between the number of charge-and-discharge cycles of a cell, and the relative cell capacity when setting the highest capacity in the early stages of a charge-and-discharge cycle to 1.0. This drawing 11 shows the software short-circuit after 50 cycles (the lithium of needlelike or arborescence penetrating a separator and being in a short circuit condition with quiet positive electrode and negative electrode) not being seen, but having a good charge-and-discharge life compared with the case of only low current discharge, in the case where the high current pulse discharge of 25 mA/cm<sup>2</sup> is performed before low current discharge of 0.2 mA/cm<sup>2</sup>.

[0024]

[Effect of the Invention] Since the charge-and-discharge cycle life of a cell can be improved by this invention and a needlelike deposit gestalt does not arise in the lithium secondary battery using a lithium metal as shown above, the industrial value is size very much.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** The coin mold cell used in the example and the example of a comparison is a sectional view a part.

**[Drawing 2]** The scanning electron microscope photograph of the negative-electrode gestalt which discharged by 0.2 mA/cm<sup>2</sup> after discharging for 30 seconds with the current density of 10 mA/cm<sup>2</sup>.

**[Drawing 3]** The scanning electron microscope photograph of the negative-electrode gestalt which discharged by 0.2 mA/cm<sup>2</sup> after discharging for 12 seconds with the current density of 25 mA/cm<sup>2</sup>.

**[Drawing 4]** The scanning electron microscope photograph of the negative-electrode gestalt which discharged by 0.2 mA/cm<sup>2</sup> after discharging for 6 seconds with the current density of 50 mA/cm<sup>2</sup>.

**[Drawing 5]** The scanning electron microscope photograph of the negative-electrode gestalt when discharging only conventional 0.2 mA/cm<sup>2</sup>.

**[Drawing 6]** The scanning electron microscope photograph of the negative-electrode gestalt which discharged by 0.2 mA/cm<sup>2</sup> and charged the pan by 0.4 mA/cm<sup>2</sup> after discharging for 6 seconds with the current density of 50 mA/cm<sup>2</sup>.

**[Drawing 7]** The scanning electron microscope photograph of the negative-electrode gestalt charged by 0.4 mA/cm<sup>2</sup> after discharging by conventional 0.2 mA/cm<sup>2</sup>.

**[Drawing 8]** The coin mold cell used for the example and the example of a comparison is a sectional view a part.

**[Drawing 9]** Drawing having shown the relation between the number of charge-and-discharge cycles of a cell, and the relative cell capacity when setting the highest capacity in the early stages of a charge-and-discharge cycle to 1.0.

**[Drawing 10]** Structural drawing of the cylindrical cell used for the example and the example of a comparison.

**[Drawing 11]** Drawing having shown the relation between the number of charge-and-discharge cycles of a cell, and the relative cell capacity when setting the highest capacity in the early stages of a charge-and-discharge cycle to 1.0.

**[Description of Notations]**

Positive-electrode case

b Negative-electrode case

c Gasket

d Lithium foil

e Positive electrode

f The separator made from polypropylene

g Positive-electrode cap

h Positive-electrode tab

i Negative-electrode tab  
k Positive electrode  
l Separator  
m Negative electrode  
n Negative-electrode can

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